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The Influence of Organic Pigments on Coating Properties

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Department of Chemical Engineering

Honors Research Project

Submitted to

The Williams Honors College

Approved:

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_____ Date _____ Reader (signed)	_____ Date _____ Dean, Honors College
_____ Reader (printed)	

Abstract

The purpose of this project was to identify the qualities of two synthesized organic pigments added to a coating. These high-performance pigments were benzodipyrrolidone and benzodifuranone, which are π-conjugated monomers. These pigments were each formulated into two different pigment concentrations and compared with a control that had no pigment. This project is limited by time constraints and the number of variables that can be tested in that time. Performance testing was conducted to evaluate the qualities of these coatings. The results demonstrated that the coatings were reproducible and most tests had results that were equal to or exceeded the results of the control. This project was worth doing because it laid the groundwork for future research that could result in an excellent corrosion and UV resistant coating. The pigments tested have potential to produce exceptional and desirable qualities to the coating in which it is imparted. This paper is submitted as part of graduation requirements for the University of Akron Williams Honors College, 2018.

Executive Summary

The purpose of this project was to evaluate two synthesized organic pigments for use in a coating. The two synthesized pigments, benzodipyrrolidone and benzodifuranone, are π-conjugated monomers which are a new class of high-performance pigments. These pigments were originally developed as dyes known for dispersibility, UV resistance, and stability and much research has been conducted over the past 40 years to enhance these properties. Both pigments make excellent backbones for building polymers that have uses as organic semiconductors that are cheaper and easier to manufacture than traditional silicon semiconductors. Due to the considerable research with these pigments, it was expected that they would carry the qualities seen in dyes and semiconductors into desirable coating qualities.

These pigments show significant promise for use in coatings. Under UV exposure, the gloss retention and thickness remain close to unchanged, and the ΔE* color change and FTIR results are equal to or better than the control results. The pull-off adhesion test results also either met or exceeded the amount of force required to remove the pull stub on the control. EIS results present a good corrosion resistance for all testing coatings. For a proof of concept of use of these pigments in coatings, the results were good and most testing met or exceeded the results of the control.

From conducting this research project, I learned several skills that will be useful in my future career. In addition to the skills I learned while on co-op, my project and time management skills have greatly improved because I needed to balance my school life with research, which can be a challenge. I learned to prioritize my time better and try to be efficient with the time I spent on my project. I became much more confident and felt a greater independence with leading my own project and I feel like this will be very useful when beginning my career. I gained better knowledge and skills in running a QUV chamber and taking gloss, thickness, color, and FTIR measurements.

I also became better acquainted with EIS testing, software, and evaluation. All of the things I learned will help me be a better engineer and a coworker that is capable of completing projects in a timely, correct, and efficient manner.

There should be future work conducted with these pigments because the results held a lot of promise. The accumulation of data from several formulations and verifying results via the use of duplicates sets a ground work for where to begin on a new project. Future work should include trying different coating types, altering the pigment concentration, investigation of other potential solvents, trying different curing temperature conditions, and investigating the differences in results between steel and aluminum as the substrate. With these potential changes, it is likely that several projects could be developed based around this work in order to find the optimum formulation for a coating containing these pigments.

My recommendations for future students working on a project similar to this seem straightforward, but are very useful and simple if they are proactive. I would recommend starting their project earlier than they think they need to so they have extra time if testing does not go according to plan. I would also recommend not choosing too many variables. Just changing one variable in a formulation results in much more work and testing than expected. If multiple variables are changed, it can be difficult to differentiate what caused the changes in results and increases the number of coating formulations dramatically. It is worthwhile to conduct a literature review early on the project so the student has a detailed understanding of the project prior to and during testing, which can lead to the student learning more from the project.

Introduction

The purpose of this project was to determine the effects of synthesized organic pigments on the properties of a coating. An epoxy resin (EPON^{TM} Resin 828) with no pigment was used as the control and two synthesized pigments, benzodipyrrolidone (BDP) and benzodifuranone (BDF), were used and compared when blended into the epoxy resin with two different pigment concentrations. To evaluate the effects of these pigments on the epoxy coatings, a series of performance tests were used to understand the differences between each pigment, as described in the **Experimental Methods** section. These pigments were chosen because both have unique electrical properties, excellent UV resistance, and are being researched for use in electronic devices. Due to their conductive properties, it was expected that this could result in a coating that would exhibit better corrosion resistance and less yellowing and chalking than epoxy resins under UV light. This project was used to determine a proof of concept and to determine if these pigments produce desired qualities in epoxy coatings. Future work will likely include varying coating types, pigment concentration, choice of solvent, curing temperature conditions, and substrate choice, either steel or aluminum.

Background

Pigmented Coatings

A pigment is a finely divided solid, which is incorporated into a medium to impart certain properties. Pigments can be inorganic or organic, colored, colorless, or fluorescent, and are typically insoluble and unaffected by the medium in which it is incorporated [1, 2]. As of 2005, 97% of produced pigments were inorganic, primarily consisting of oxides, sulfides, silicates, sulfates,

and carbonates [2]. There are several reasons for adding a pigment to a coating, including enhancing physical properties (e.g. corrosion mitigation), altering costs (e.g. low-cost filler), imparting color, and affecting appearance [3, 4].

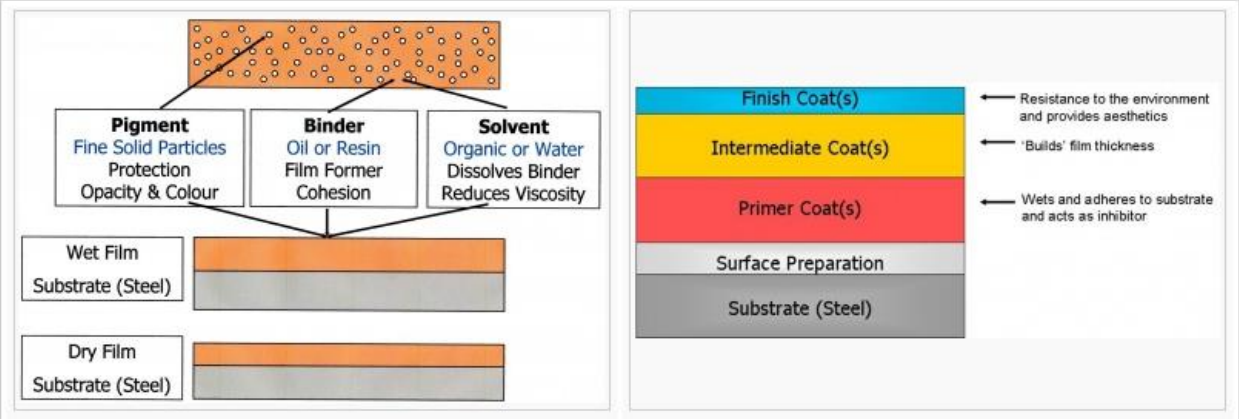

Figure 1: (a) Paint constituents and their function (b) Schematic diagram of a paint system [3].

As seen in **Figure 1**, the pigment works together with the rest of the coating and can be found in the finishing, intermediate, and primer coats depending on the purpose of the coating.

Pigments have been used by humans for imparting color for thousands of years. Cave paintings typically used yellow and red ochre, white chalk, and carbon black from soot of burned animals [5]. Tyrian Purple was one of the most complicated pigments to make, as it utilized the mucus from thousands of Murex snails, making it very costly [5]. In 1704, the first chemically synthesized color, Prussian Blue, was produced by Diesbach, a German color maker [5]. In the late 18th century, newly isolated elements were able to produce new pigments at a low cost, including zinc oxide and chrome [5]. The addition of pigments in coating to impart qualities used other than just for visual appeal began around World War II. DayGlo fluorescent paints would fluoresce under black light and daylight conditions and were used during WWII for a variety of signaling purposes [5]. Corrosion inhibitive pigments were first fully utilized during WWII on ships [7]. The most widely

used pigments were various kind of zinc and lead chromates, which are highly effective corrosion inhibitors [7]. From WWII to now, pigments have been developed to be extremely versatile and capable of adding physical properties to produce a more robust coating.

Pigment Synthesis

The two synthesized pigments examined in this paper are benzodipyrrolidone (BDP) and benzodifuranone (BDF), which are π-conjugated monomers and derivatives of diketopyrrolopyrroles (DPPs), which are a new class of high-performance pigments, obtained from BASF Corporation [8, 9, 10]. The alternating donor-acceptor architecture of conjugated polymers allows for many possibilities for desired properties by combining different donors and acceptors [9]. BDP, BDF, and DPPs are used as backbones in the development of compounds with high charge mobility to be used in electronic devices and coatings [8, 9]. DPPs are made by reacting benzonitrile with dialkyl succinate in the presence of alkali metal tertiary alkoxides as bases [11]. A Reformatsky reaction of the succinate with benzonitrile produces a diester, with best results occurring with the use of succinates of tertiary or secondary alcohols [11]. The rate of reaction is increased with temperature and succinate concentration [11]. Most DPP derivatives are synthesized by reacting a succinate ester and benzonitrile derivatives via a cyclization [12]. The chemical structures of DPP, BDF, and BDP are displayed in **Figures 2**, **3**, and **4**.

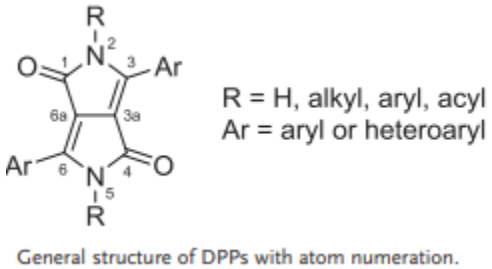

Figure 2: Chemical structure of DPP [11].

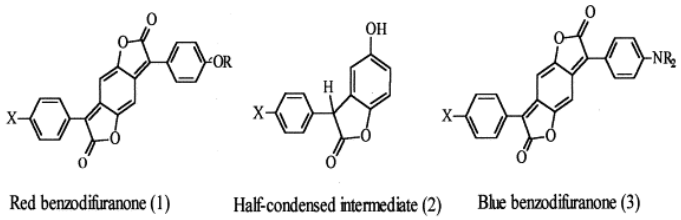

Figure 3: Different pigment colors of BDF [13].

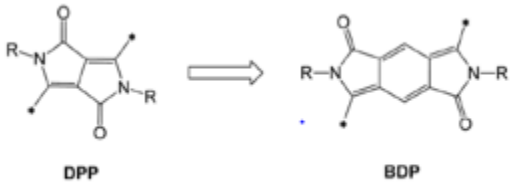

Figure 4: Chemical reaction from DPP to BDP [14].

Potential Applications

DPP, BDP, and BDF were originally synthesized as organic, low solubility dyes in the 70s and 80s and were well known for robust, vibrant, and long-lasting color [9]. DPP-containing polymers have photovoltaic and light-emitting properties [15]. BDP and BDF, among other π-conjugated polymers, were developed from DPP to have a broad absorption range, high electron and hole mobility, high flexibility, and low cost, and have been identified for potential uses in organic photovoltaics (OPVs), organic field-effect transistors (OFETs), and organic light-emitting diodes (OLEDs) [9, 15]. Polymer semiconductor mobility is typically 0.1 $cm^2 V^{-1} s^{-1}$ [14]. In BDP, small gap polymers can be produced by combining quinoid structures with aromatic monomers, favoring high charge mobility [9]. BDP-based polymers have been reported to have carrier charge mobilities up to 0.03 $cm^2 V^{-1} s^{-1}$ for holes and 0.012 $cm^2 V^{-1} s^{-1}$ for electrons in OFETs and would be a useful acceptor building block when used in polymer semiconductors [9, 14]. Semiconductors that are made from π-conjugated polymers are expected to be key elements in display technologies and other

electronic devices because they are superior to silicon-based semiconductor materials due to flexibility, lightweight, low-cost, and processability [17].

Potential Applications in Coatings

BDF and BDP are high class performance pigments that have been developed and improved over that last 40 years. Both pigments have deep colors, are UV resistant, and have an innate stability that made them excellent dyes, used specifically for polyesters [10, 14, 16, 18]. For use in dyes, both pigments were easily dispersible which is important in achieving a uniform color and appearance in a coating. Pigments that are used in finishing coatings must protect the binder and substrate from UV radiation, among other things, to ensure the long-term performance of the substrate and coating [19]. Due to the desirable properties seen in dye formulations, it was expected that BDF and BDP would carry these properties into an epoxy coating and would resist the yellowing an chalking commonly seen in epoxy coatings not protected by polyurethanes.

Design

Cost

π-Conjugated polymer semiconductors have applications in organic printable electronics and commercial pigments because of their stability and cost [10]. Silicon wafers, which are thin slices of semiconductor material, are currently used in most electronics, including photovoltaics, field-effect transistors, and light-emitting diodes. There is a shortage of these wafers due to increasing demands in technology, which leads to increased prices. The current cost of a 2-inch silicon wafer with a 0.5mm thickness is $421 for 5 wafers on Sigma-Aldrich and these prices are expected to increase in the foreseeable future [21]. Due to the increasing price of silicon wafers, the use of π-conjugated polymer semiconductors, like BDF and BDP, in electronics could be a huge cost saver.

According to Sigma-Aldrich, the average cost of π-conjugated polymers is roughly $300-$400 per gallon, which would have a lower cost and less of a limited supply when compared to silicon wafers [20]. Advantages of BDF and BDP over silicon-based semiconductor materials includes their flexibility, lightweight, low-cost, and processability [17]. The biggest constrains to using pigments like BDF and BDP in OPVs, OFETs, and OLEDs is the development of the ideal chemical additions to the backbone of the π-conjugated polymers, of which there is a large amount of research but limited industrial implementation.

Epoxy coatings are traditionally used in a two-coat system with epoxy as the base layer and a UV-resistant polyurethane top coating [22]. Producing a single-coat epoxy coating that has UV-resistant properties by incorporating pigments such as BDF and BDP can result in significant cost savings [22]. Epoxy coatings have uses in a variety of applications including military, maritime, aeronautical, automotive, and general business organizations [23]. Some applications are not exposed to UV light, but when epoxy is exposed to UV light it can result in yellowing and chalking. Polyurethane initially costs slightly more than epoxy coatings, but traditionally lasts longer than epoxy coatings alone [24]. The production of an epoxy that does not need a polyurethane top coating but results in similar properties would decrease the overall cost of instillation of an epoxy coating system. For use in floor coatings, polyurethane top coats can cost between $4-$6 per square foot, where an epoxy coating costs between $2-$4 per square foot [25]. A system that only needed an epoxy coating could cost at least half as much. The global demand for high performance pigments is expected to continue to rise through 2022, where the market is expected to be worth $17.58 billion [26]. Due to these increasing market sales, the cost of high performance pigments has dropped dramatically since 1999. DPP red was $50/lb 19 years ago, where today the cost has dropped to 20-50% of that price, partly due to the end of patent induced monopolies [26]. The added

cost of DPP based pigments relies heavily on the pigment volume concentration (PVC) used in the coatings, for this study 2% and 4% PVC was tested. As seen in the **Data and Results** section, the 4% PVC had only slightly better results compared to 2%, indicating that the lower amount of pigment would be adequate to produce improved UV-resistance. At a cost of $10-$25/lb for the pigment, the addition of small amounts of pigment to the coating would still cost significantly less when compared to a two-coat polyurethane-epoxy system.

Safety

DPPs are organic pigments that come in the form of particles and thus pose a risk of inhalation and are flammable. An animal study compared the health effects of five DPP-based pigments to inorganic Pigment Red 101 [31]. Rats were exposed to the particles for 6hr/day for 5 days in a row, with concentrations of 30mg/m^3 in order to determine the toxicity of each compound, following a 3-week recovery period using broncho-alveolar lavage fluid (BALF) [31]. At the end of the study, it was determined that all of the test subjects tolerated the exposure well and did not undergo significant changes to the DPP pigments [31]. The inorganic pigments saw more pigment deposition and pigment phagocytosis, but the test subjects also healed completely [31]. In addition to this study, a MSDS sheet for Verdcol® DPP Red 254 PTR describes the pigment as containing no ingredients/impurities classified as hazardous to health according to EU and UK chemicals legislation [32]. Another MSDS sheet for DPP Pigment Orange 71 contains further health and safety warnings [27]. This pigment may form a combustible dust concentration in the air and could cause allergic skin reactions [27]. It is advised for this pigment to be decanted into smaller, more manageable containers under a hood with good ventilation and should be stored in dry, cool, ventilated areas with measures taken against static discharges because it is classified as dust explosion class 2 [27]. This pigment is incompatible with strong oxidizing agents, strong bases,

and strong acids [27]. According to these three sources, DPPs are reasonably safe, do not pose an inhalations threat, and should be used with typical laboratory precautions, including gloves, eye protection, lab coat, and chemical hood.

The largest safety concern with using DPP pigments in epoxy coatings is the EPON™ Resin 828 and curing agent, EPIKURE™ 3164. The EPON™ Resin 828 has been identified to have skin corrosion/irritation, serious eye damage/ eye irritation, skin sensitization, and specific target organ toxicity in a single exposure to the respiratory tract [28]. EPIKURE™ 3164 has been identified to be harmful when in contact with skin or if swallowed, and causes eye burns, respiratory tract and skin irritation and may cause allergic respiratory and skin reactions [29]. As long as the chemicals used to make these epoxy coatings with DPP pigments are stored and handled according to the SDS instructions, there should be little risk to individuals using these chemicals.

Regulations and Environmental

Regulations and environmental risks associated with DPPs are much less than other alternatives used in coatings and electronics. DPP epoxies have had increasing use in the automotive market [30]. In recent years, the automotive market has looked towards more sustainable business practices, which also includes coatings. Traditional inorganic coatings, especially lead chromates and heavy metal ions, have become less popular due to the risk they pose to humans and the environment when compared to organic pigments [30]. DPP based pigments can be used in solvent, water, and powder pigments, which allows for more environmentally friendly coatings to be developed with lower volatile organic compounds (VOCs) that will be compliant with REACH standards that are beginning to go into effect [30]. REACH is a new set of regulations set by the European Union to improve the protection of human health and environment from risks posed by chemicals and stands for registration, evaluation, authorization, restriction, and communication in the supply chain. Due

to the amount of influence the European market has, many US companies are also working on becoming REACH compliant in order to sell their products in an international market. High performance organic pigments have become a higher quality product with less environmental impact than oxide mining, especially iron oxide mined in China [30].

In addition to regulations seen in coatings, the amount of regulation associated with currently used silicon semiconductors is much more significant when compared to DPP-based electronics, especially when considering environmental concerns. In the manufacturing process of metallic semiconductors, approximately thirty air toxics are emitted, 90% of those emissions are hydrochloric acid, hydrofluoric acid, glycol ethers, methanol, and xylene [33]. The EPA has set emission regulations to handle the toxins from process vents and storage tanks, with separate vents for organic and inorganic substances [33]. Organic air toxins must be below 20 ppm by volume and inorganic air toxins must be below 0.42 ppm by volume [33]. DPPs are regulated by the Environmental Protection Act 1990 and the Pollution Prevention and Control Act 1999 [32]. These polymers should not be dumped down drains, waterways, or areas where ground and surface water would be affected and should be disposed of according to regulations, along with contaminated packaging [32]. According to OSHA, DPP acceptable limits are total dust of 15 mg/m^3 and respirable amounts of 5 mg/m^3 [32].

Experimental Methods

Coating Formulation

The epoxy resin (EPON^{TM} Resin 828) and curing resin (EPIKURE^{TM} Curing Agent 3164) were obtained from Hexion Specialty Chemicals, with the weight ratio of curing agent to resin is 1.36.

BDF and BDP were dispersed in acetone by stirring for 5 minutes at 1000 rpm, the EPON™ Resin 828 was added and mixed mechanically for 10 minutes, followed by EPIKURE™ Curing Agent 3164 and mixed for an additional 10 minutes. The coating was applied to an aluminum test panel that was cleaned with acetone and DI water, with a 127µm wet film thickness. The coatings were dried over night at room temperature, then cured for 2 hours in the oven at 100 °C. The different coating formulations are displayed in **Table 1**.

Table 1: Coating formulation table.

Formulation Name	Pigment Volume Concentration
E0	0%
EF2	2%
EF4	4%
EP2	2%
EP4	4%

Performance Testing

To evaluate the performance of the pigments and coatings, a series of performance tests were conducted over the course of 24 to 38 days depending on the test. The primary test conducted was UV testing performed using a QUV chamber. Each sample was run in duplicate and was exposed to constant UV light for 24 days. Results were measured initially and after 1, 3, 7, 14, and 24 days. Gloss, thickness, and color measurements were performed on each sample. Gloss measurements were taken on three different locations on the panel and 20°, 60°, and 85° measurements were recorded. The data is presented in gloss retention, which is the average 24-day data divided by the average initial data to best demonstrate the change over time. Thickness measurements were taken on ten different locations on each panel, neglecting the outer 1/4”, and an average was calculated for each panel. Color measurements were taken on one location on each panel and L*, a*, and b*

measurements were recorded using CIELAB, which is color space specified by the International Commission of Illumination to describe all colors visible to the human eye [34]. L* describes the brightness or lightness going from white to black, a* indicates the colors from green to red, and b* indicates the colors from blue to yellow, displayed in **Figure 5** [34]. These values are used to obtain ΔE* using the CIELAB 1976 color space equation,

$$\Delta E^*_{ab} = \sqrt{(L^*_2 - L^*_1)^2 + (a^*_2 - a^*_1)^2 + (b^*_2 - b^*_1)^2} \quad (1)$$

where ΔE*≈2.3 is the just noticeable difference to the human eye [34].

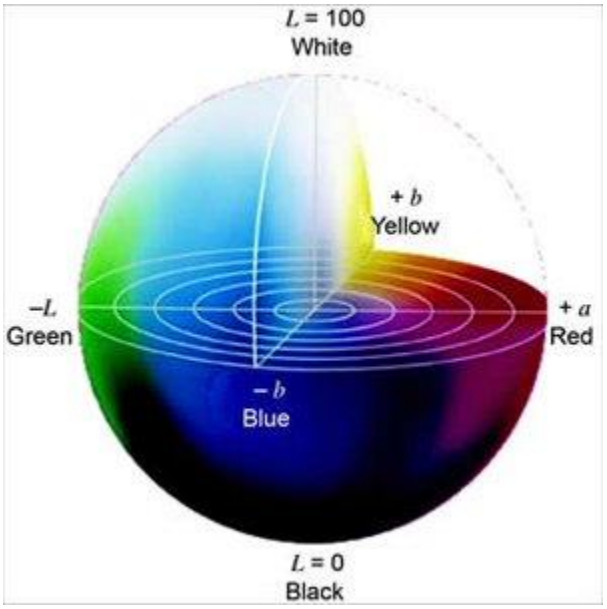

Figure 5: CIELAB color space visual model [35].

Fourier transform infrared (FTIR) was the last testing performed on the UV samples and results were measured initially and after 24 days. The data is displayed with the % transmittance, indicating which chemical compounds are present in the coating and can help to determine what part of the pigment is degrading.

Pull off adhesion testing was performed five times for each sample. The day prior to testing, a thin coating of epoxy was applied to the flat face of the pull stub and placed firmly on the sample. After 24 hours, the pull stub is inserted in the mechanical pull off device and the amount of pressure in psi was recorded and averaged, as displayed in **Figure 6**.

Figure 6: DeFelsko PosiTest AT-A Automatic Pull-off Adhesion Tester (left) Cross sectional view of pull stub in pull off actuator (right) [36].

EIS testing was performed on each sample with several duplicates over 38 days. Results were measured after 30 minutes, 1 day, 3 days, 7 days, 14 days, 24 days, and 38 days. The test set up is displayed in **Figure 7**, where the coated substrate has the hollow cylinder filled with electrolyte, in this case it was 3.5wt% NaCl, clamped to the panel for the duration of the test, which is conducted with a platinum mesh counter electrode, and results are collected inside a Faraday cage. The impedance (Zmod) is collected and normalized with the area of the sample.

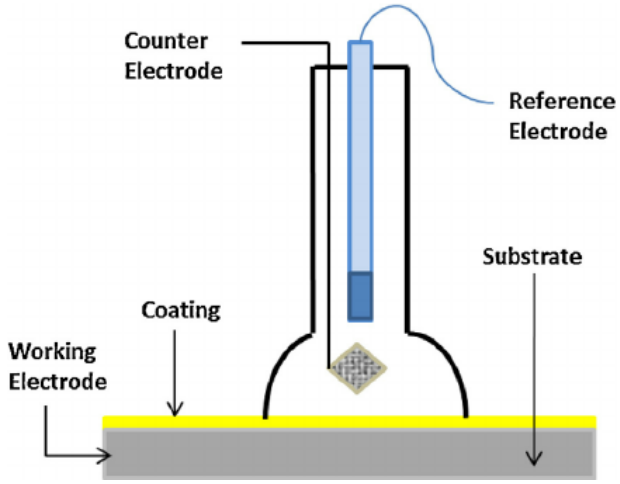

Figure 7: EIS testing set up for a substrate with a coating [37].

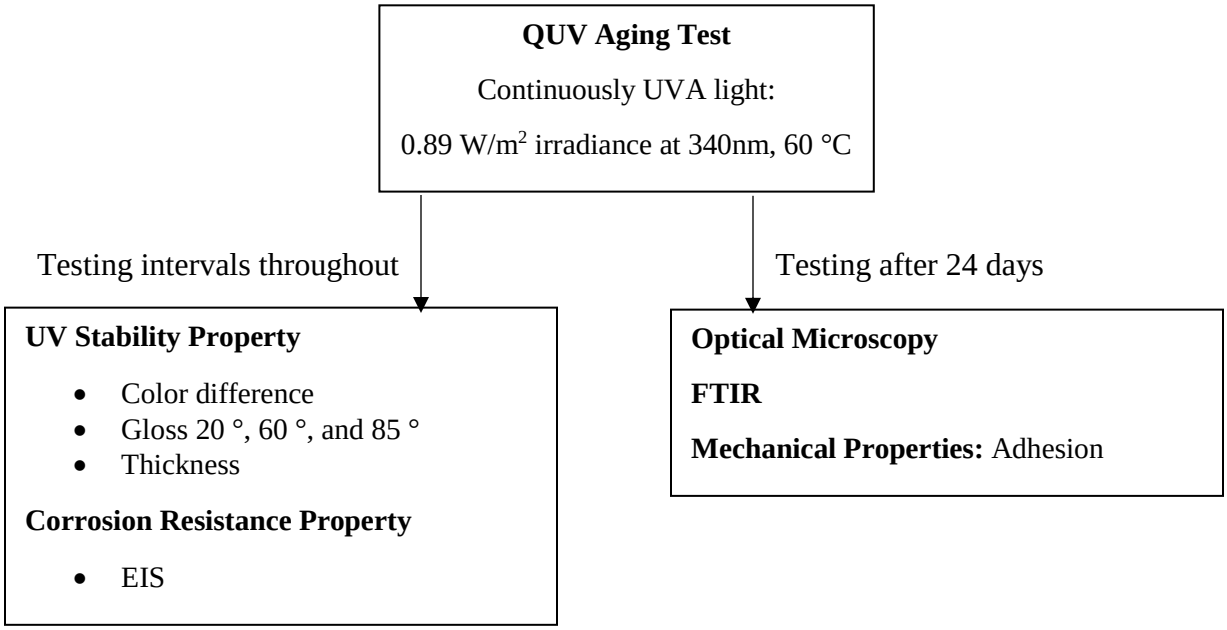

Figure 8: Test protocol used for all coating samples.

Data and Results

Thickness

The change in thickness measurements for both duplicates are displayed in **Figures 9** and **10**. Thickness measurements were run in duplicate and averaged over ten different locations on each panel. The results between duplicates line up closely, showing repeatability between samples. The BDP formulation EP4 has the biggest difference between initial and 24 days results, with 6µm change compared to the control with 2µm change.

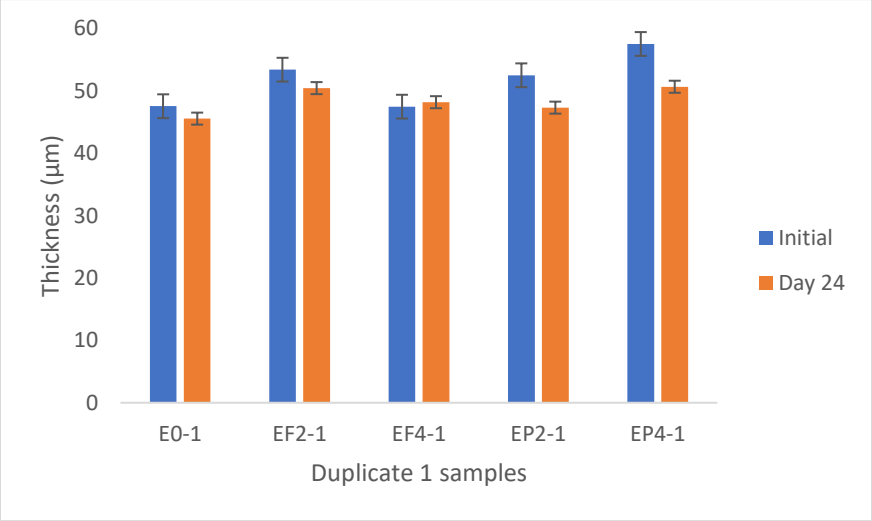

Figure 9: Coating thickness measurements of all five samples comparing initial and after 24 days UV exposure for duplicate 1.

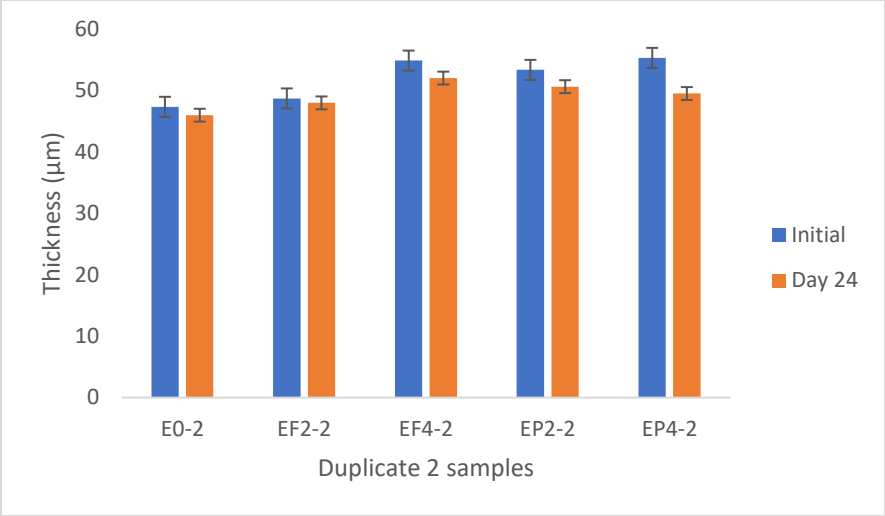

Figure 10: Coating thickness measurements of all five samples comparing initial and after 24 days UV exposure for duplicate 2.

Color Change

ΔE* color change results and duplicates are displayed in **Figures 11** and **12** and **Table 2**. Color measurements L*, a*, and b* were recorded using CIELAB and ΔE* values were calculated according to **Equation 1**. The best results are ones that have the smallest change over time. Similarly to the thickness results, the duplicates line up closely showing repeatability between samples. The BDP formulations EP2 and EP4 change initially, but level off after about 5 days and have very little change after that point.

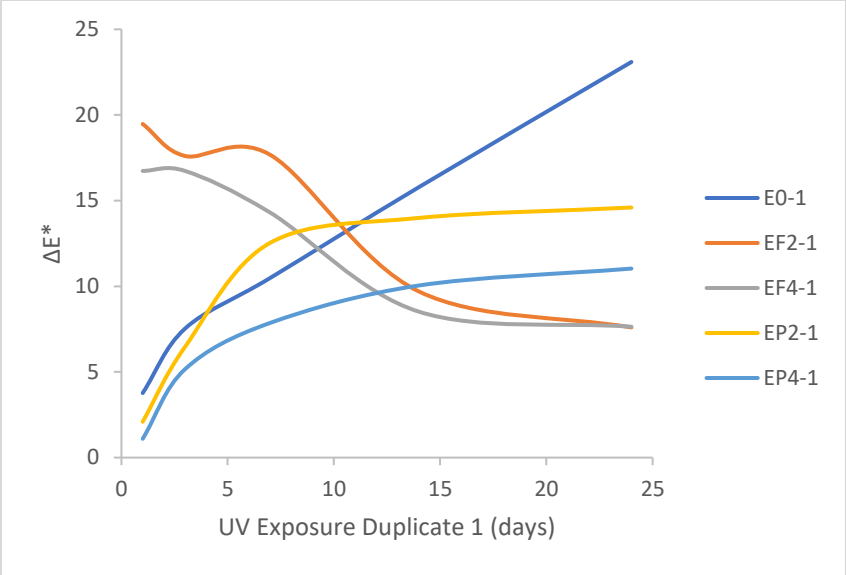

Figure 11: ΔE* after UV exposure of all five samples over 24 days for duplicate 1.

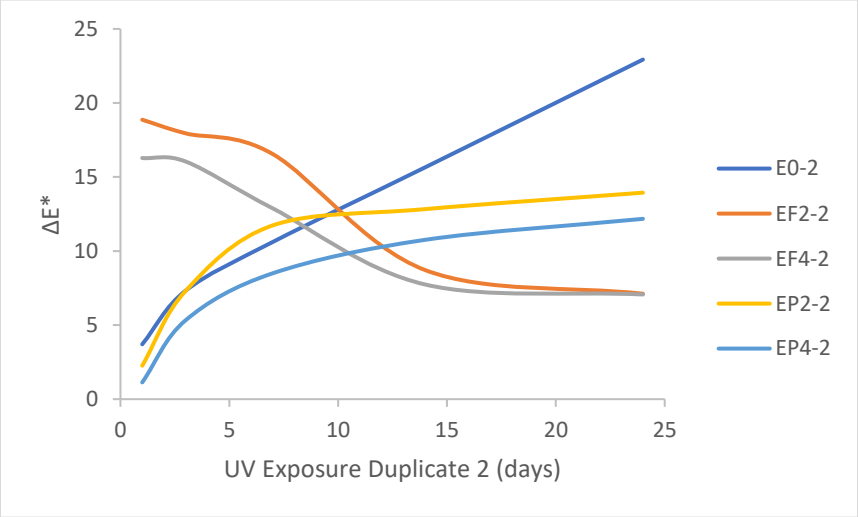

Figure 12: ΔE* after UV exposure of all five samples over 24 days for duplicate 2.

Table 2: ΔE* values used to generate **Figures 11** and **12**, where the bold, italic values are below the just noticeable difference to the human eye value of 2.3.

	Duplicate 1				
Coatings	ΔE*	ΔE*	ΔE*	ΔE*	ΔE*
	Day 1	Day 3	Day 7	Day 14	Day 24
E0-1	3.77	7.54	10.48	15.79	23.09
EF2-1	19.47	17.60	17.67	9.70	7.60
EF4-1	16.73	16.73	14.30	8.52	7.64
EP2-1	***2.09***	6.47	12.54	13.99	14.60
EP4-1	***1.10***	5.17	7.86	10.05	11.03
	Duplicate 2				
Coatings	ΔE*	ΔE*	ΔE*	ΔE*	ΔE*
	Day 1	Day 3	Day 7	Day 14	Day 24
E0-2	3.71	7.33	10.62	15.66	22.93
EF2-2	18.87	17.95	16.55	8.72	7.12
EF4-2	16.28	16.04	12.88	7.74	7.07
EP2-2	***2.26***	7.32	11.74	12.83	13.94
EP4-2	***1.13***	5.34	8.50	10.76	12.18

Gloss

The gloss data is presented in gloss retention, which is the average 24-day data divided by the average initial data, is seen in **Figures 13** and **14**. Gloss retention between the duplicates has similar results for each sample except for BDP formulation EP2 duplicate 1, which has significantly lower 20° and 60° gloss. Gloss retentions that were above 90% displayed acceptable results.

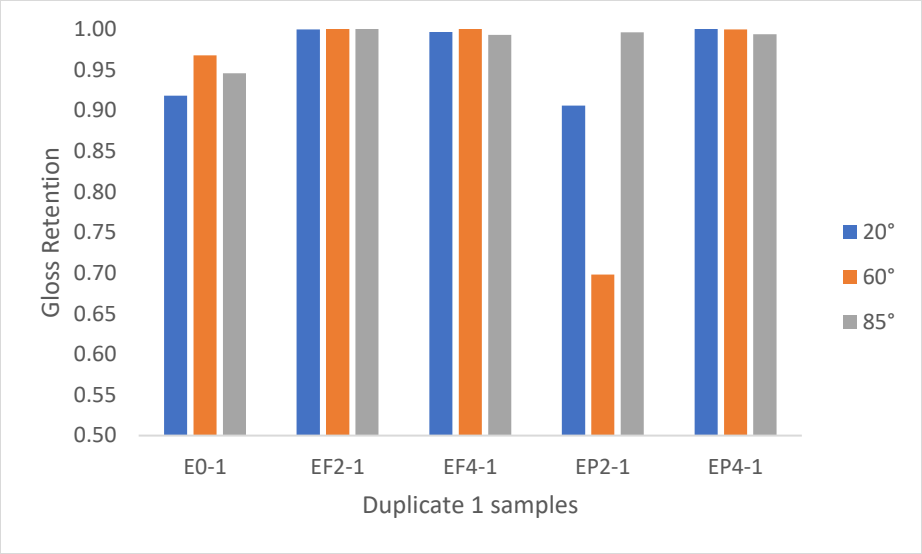

Figure 13: Gloss retention measurements of all five samples after 24 days UV exposure for duplicate 1.

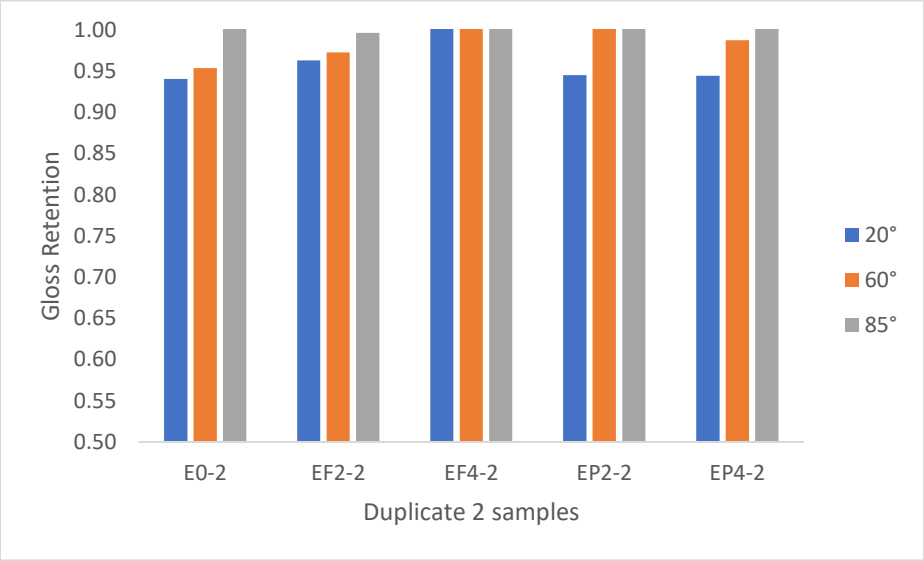

Figure 14: Gloss retention measurements of all five samples after 24 days UV exposure for duplicate 2.

FTIR

The FTIR data is displayed with the % transmittance, displayed in **Figures 15-19**. The change on transmittance indicates which chemical compounds are present in the coating and can help to determine what part of the pigment is degrading. FTIR data between duplicates display similar changes in a transmittance, duplicate data is in the **Appendix**. The control displayed a larger change between the initial and 24-day results. The area between 3500-3250nm is the OH region, 3000-2750nm is N-H, 1750-1500nm is N-H and C-OH, and 1250-1000nm is C-O-C. The changes in these areas could be the results of the degradation of the compounds found in these regions [29].

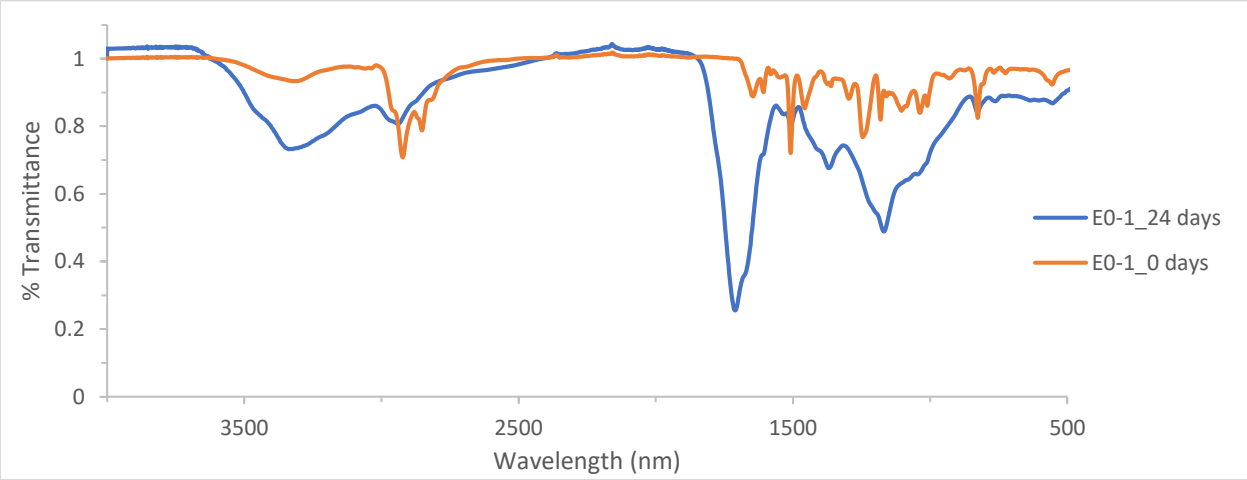

Figure 15: FTIR data for the control comparing the absorbance data initially and after 24 days of UV exposure for duplicate 1.

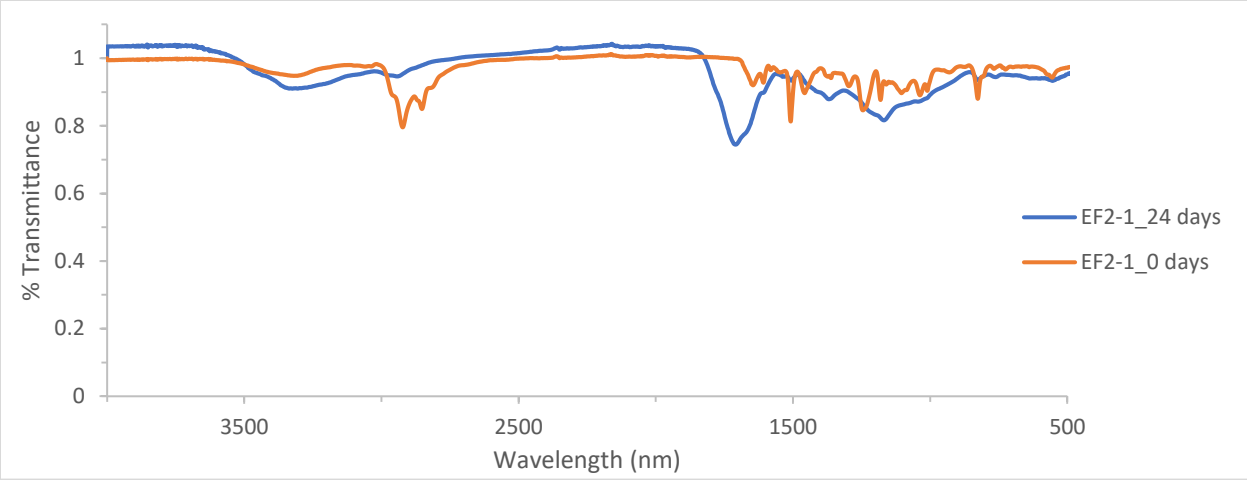

Figure 16: FTIR data for BDF formulation EF2 comparing the absorbance data initially and after 24 days of UV exposure for duplicate 1.

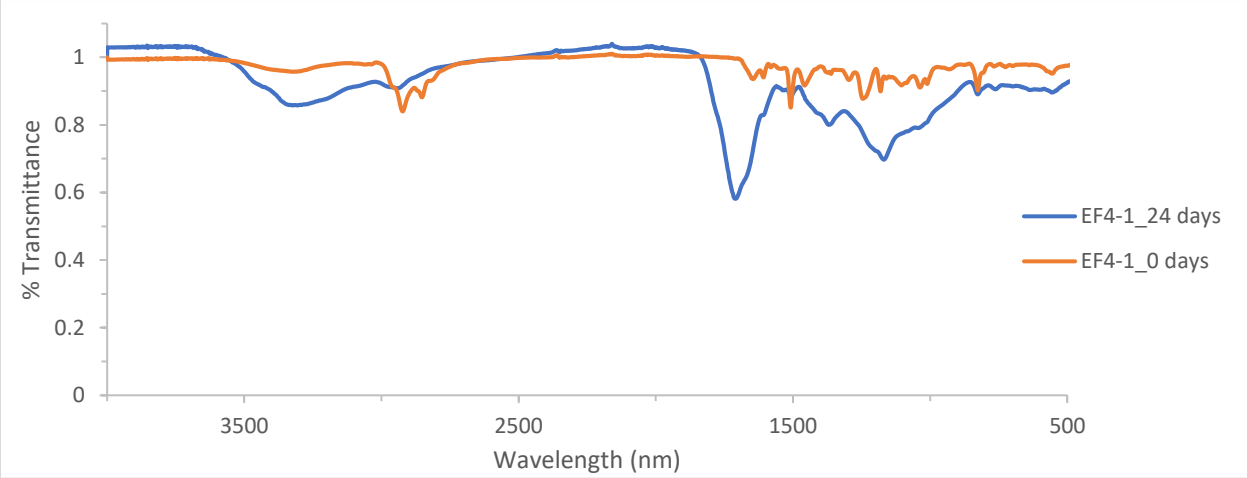

Figure 17: FTIR data for BDF formulation EF4 comparing the absorbance data initially and after 24 days of UV exposure for duplicate 1.

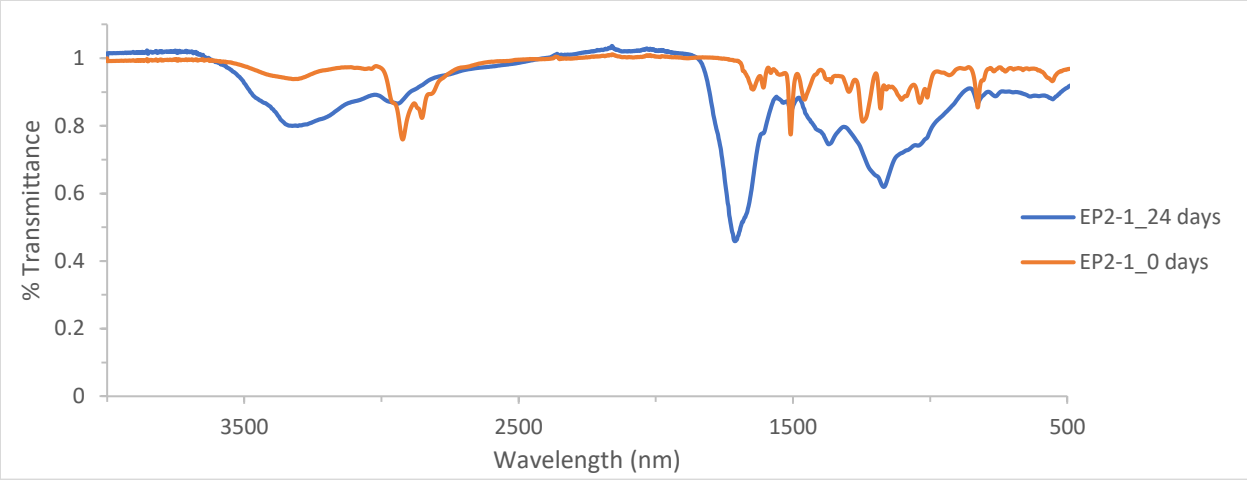

Figure 18: FTIR data for BDP formulation EP2 comparing the absorbance data initially and after 24 days of UV exposure for duplicate 1.

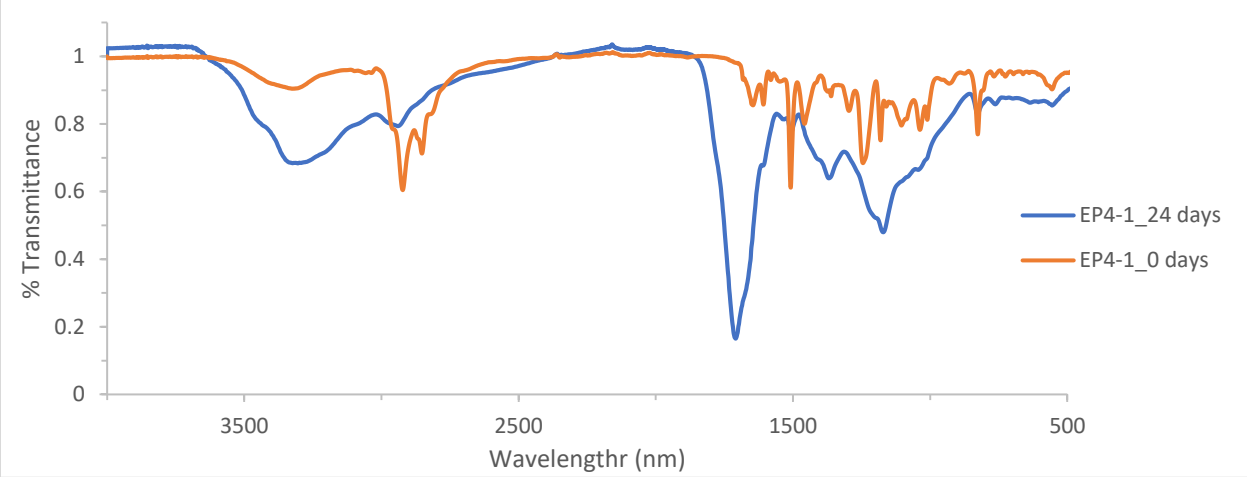

Figure 19: FTIR data for BDP formulation EP4 comparing the absorbance data initially and after 24 days of UV exposure for duplicate 1.

Adhesion

Pull off adhesion testing is displayed in **Figure 20**. Each sample was tested before UV exposure five times per sample and averaged. All samples are in a similar range to the control.

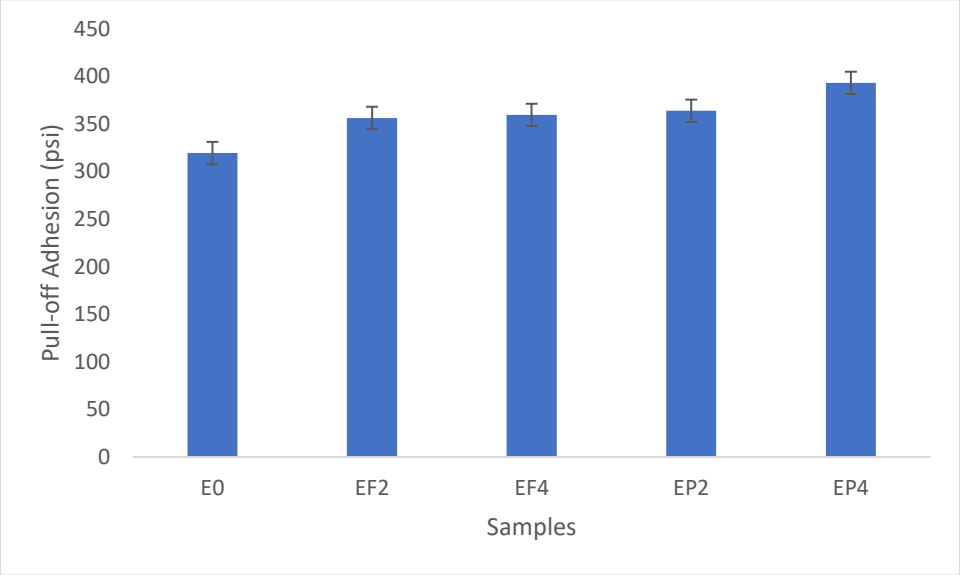

Figure 20: Pull-off adhesion strength value of different formulation samples.

Electrochemical Impedance Spectroscopy

EIS testing was performed on each sample over 38 days, seen in **Figures 21-25**. The impedance (Zmod) is collected and normalized with the area of the sample. It is important to take into account starting impedance and how quickly it takes for it to decline.

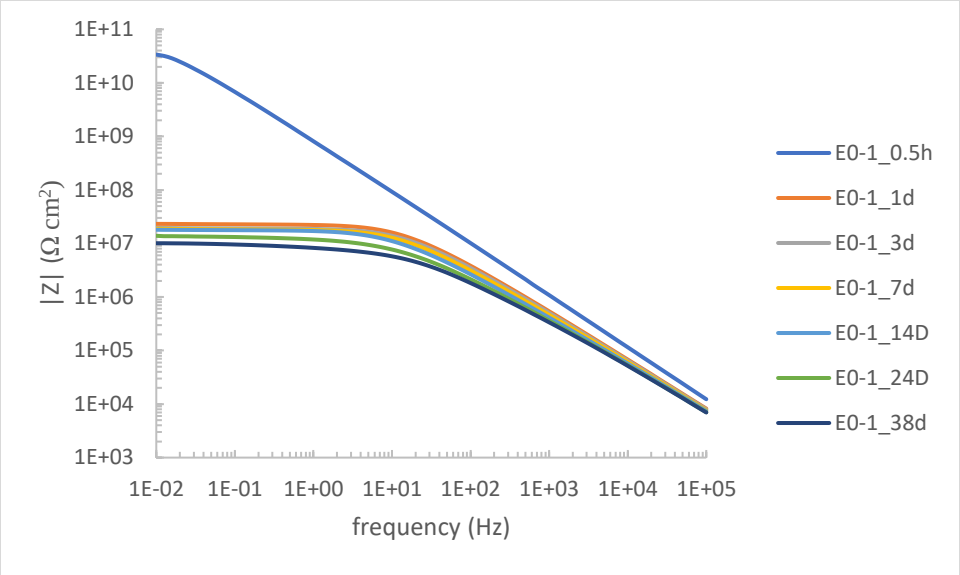

Figure 21: Bode plots (impedance modulus) of coating samples before and after different UV exposure time for the control.

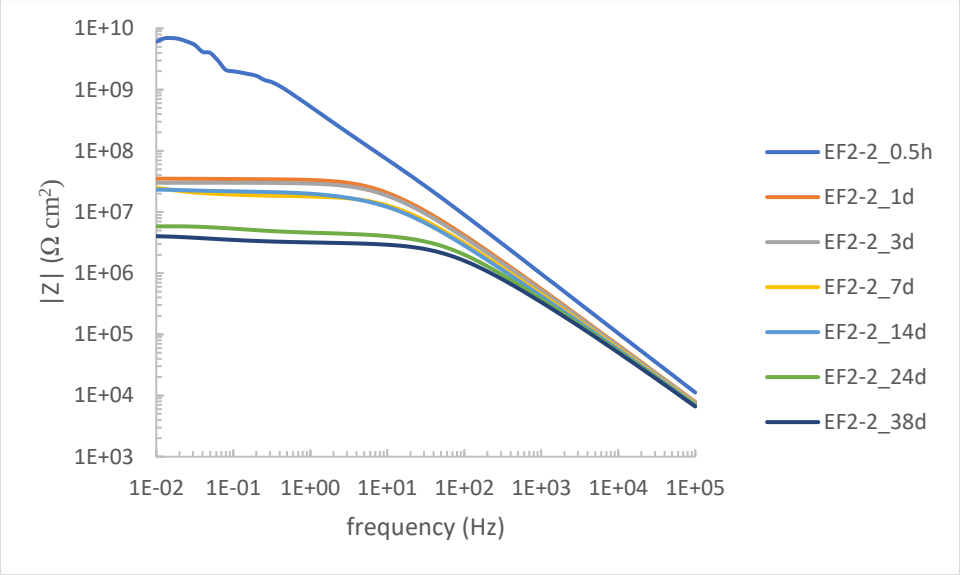

Figure 22: Bode plots (impedance modulus) of coating samples before and after different UV exposure time for the control BDF formulation EF2.

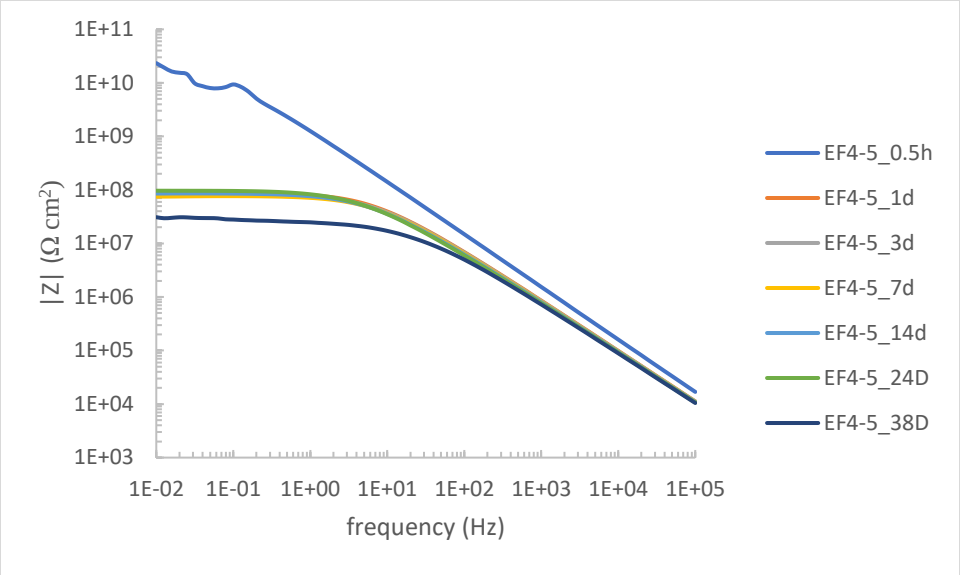

Figure 23: Bode plots (impedance modulus) of coating samples before and after different UV exposure time for the control BDF formulation EF4.

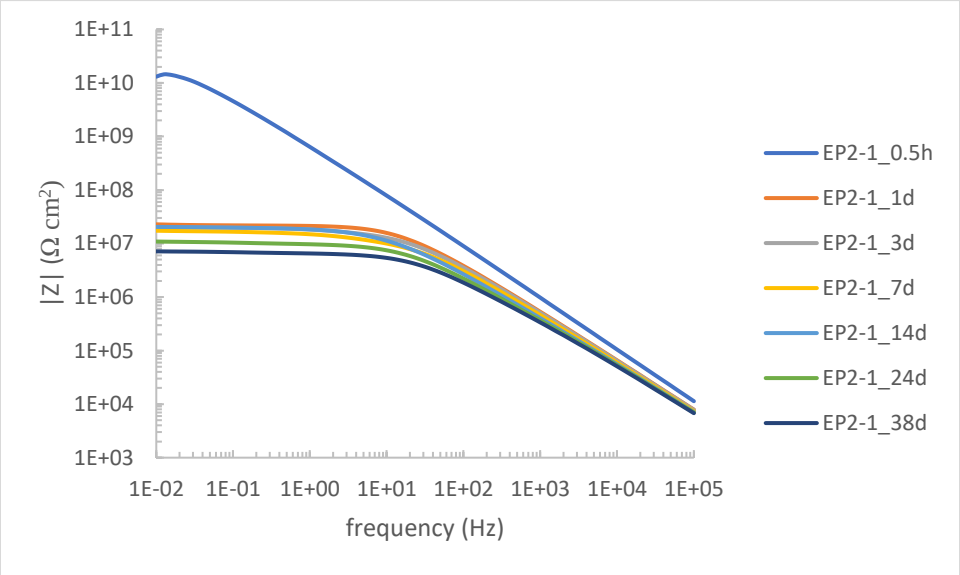

Figure 24: Bode plots (impedance modulus) of coating samples before and after different UV exposure time for the control BDP formulation EP2.

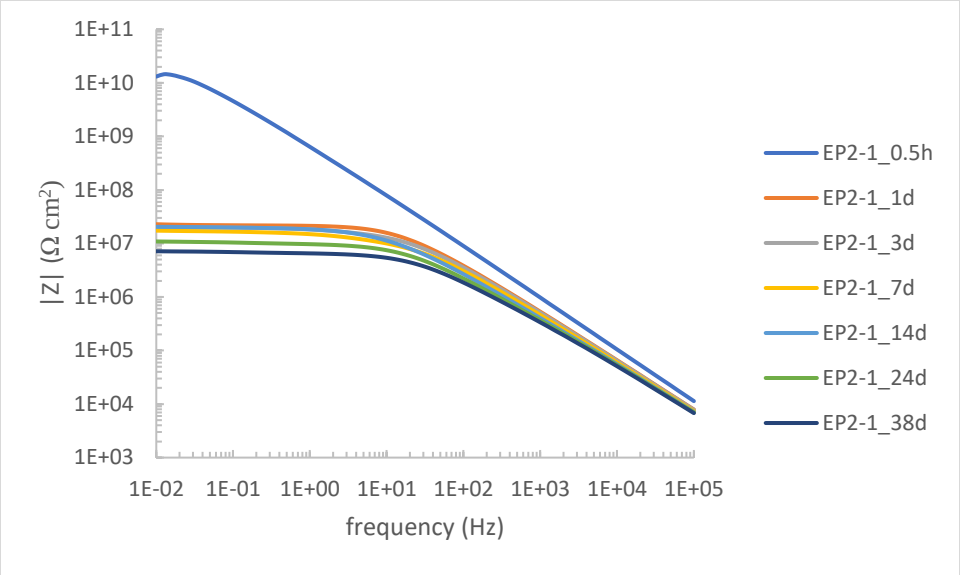

Figure 25: Bode plots (impedance modulus) of coating samples before and after different UV exposure time for the control BDP formulation EP4.

The impedance at 0.01Hz normalized to the area helps to display how quickly the impedance drops off over time and how similar the coatings are, as seen in **Figure 26** and **27**. The control initially displayed the best results but became equal with the rest after 3 days.

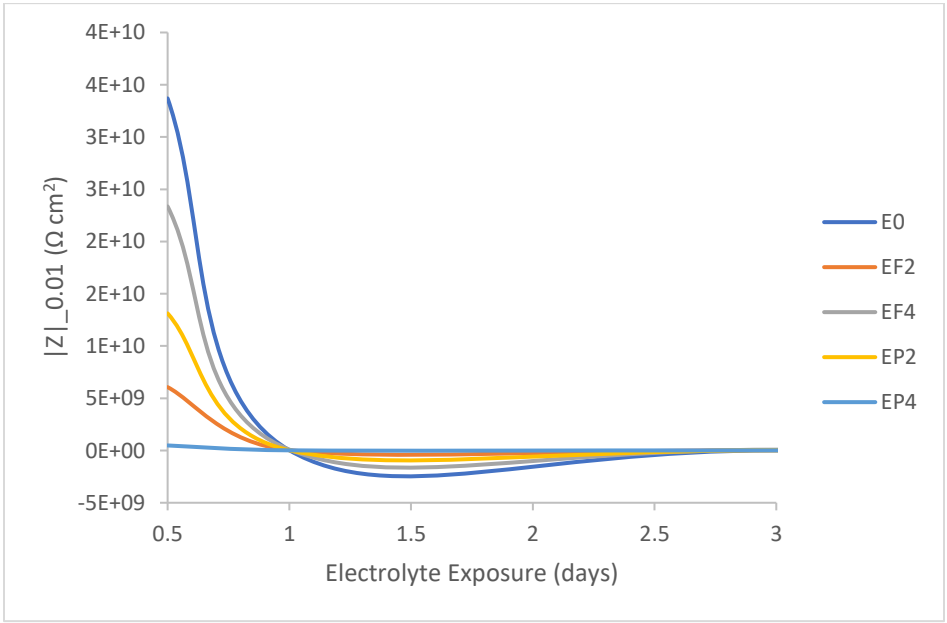

Figure 26: The impedance modulus at low frequency (0.01 Hz) as a function of UV exposure time.

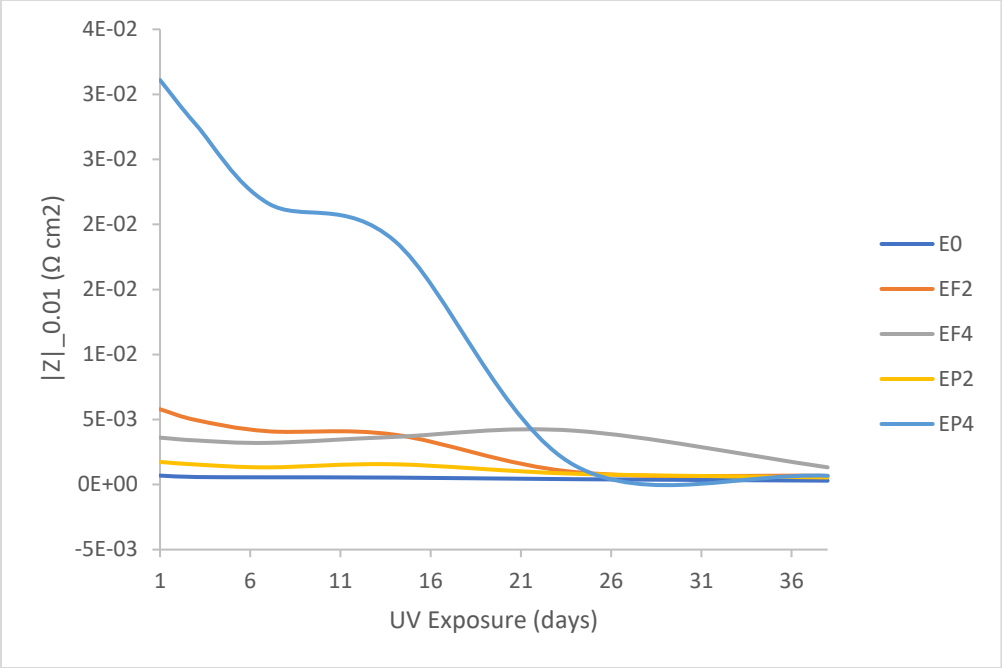

Figure 27: Relative data where |Z|0.01 HZ_day(t)/|Z|0.01HZ_day (0) as a function of UV exposure time.

Discussion, Analysis, and Conclusions

Each of the tests displayed in the **Data and Results** section was purposely run in duplicate or more in order to obtain more accurate results and to see if there was any reproducibility between the same samples. For thickness, color, and gloss retention, the duplicates appeared the same or very close for all samples excluding BDP formulation EP2 duplicate 1 gloss retention, which had significantly lower 20° and 60° gloss. It would be worth while to repeat that test to see if it was a random occurrence or if it always has varying results. The thickness measurements were good overall, where BDP formulation EP4 has the largest difference between initial and 24 days results, with 6µm change compared to the control with 2µm change. The nearly all the color change results were above the just visible to the human eye threshold of 2.3 after one day, and all were above that at the end of testing. Several of the samples began to level off between the middle and end of the

testing, which is a good sign despite the large initial changes in ΔE*. The FTIR data changes were similar for the BDF and BDP formulations, which had less change than the control. Based on the comparison between the control and formulations, it would appear that the addition of the pigment helped to increase the UV stability. The pull-off adhesion results were all in the 300-400 psi range with all of the samples meeting or exceeding the control. It appears that all of the EIS testing produced similar results between the coatings. There is a significant drop in impedance between 0.5 hours and 1 day for all samples, showing the breakdown of the barrier properties of the coatings. It would appear that the addition of the pigments did not affect the barrier properties.

From this experiment, I learned how to develop an effective testing plan, draw conclusions from the results, and develop a better understanding of the effect that each formulation variable has on the testing results. This is helpful in fine tuning the formulation of the coating for any future work involving these pigments or similar work. By accumulating data for a variety of formulations, a new idea for a future project could be developed based upon the testing completed. From there, the groundwork for the new project could be laid out, allowing others to develop new coatings for a potentially different purpose and gaining a better understanding of the synthesized pigments produced which could lead to their future use. Pigments have come a long way from just adding color to a coating and are an important aspect in any corrosion mitigation system.

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Appendix

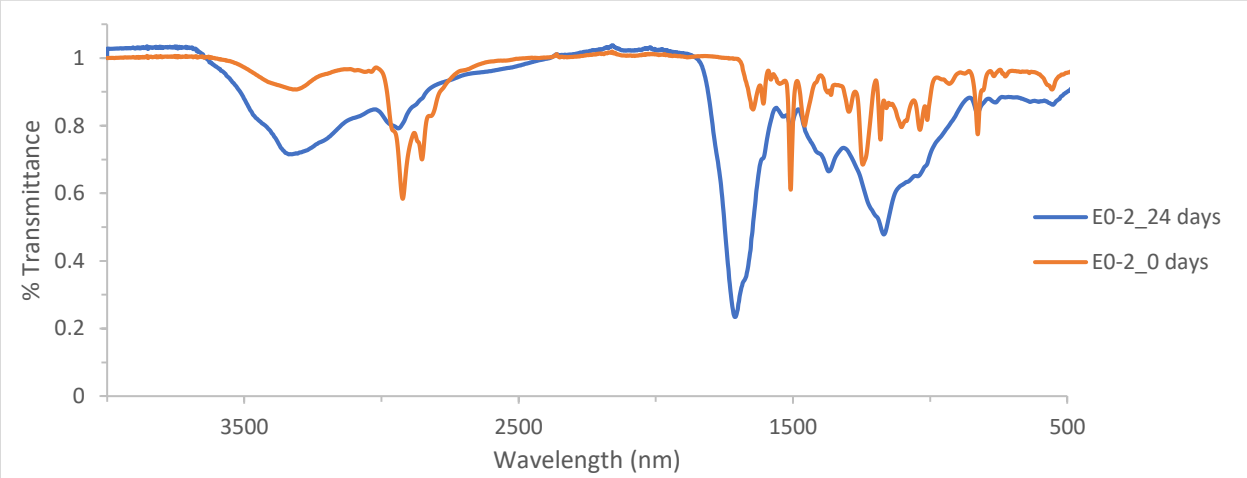

Figure A1: FTIR data for the control comparing the absorbance data initially and after 24 days of UV exposure for duplicate 2.

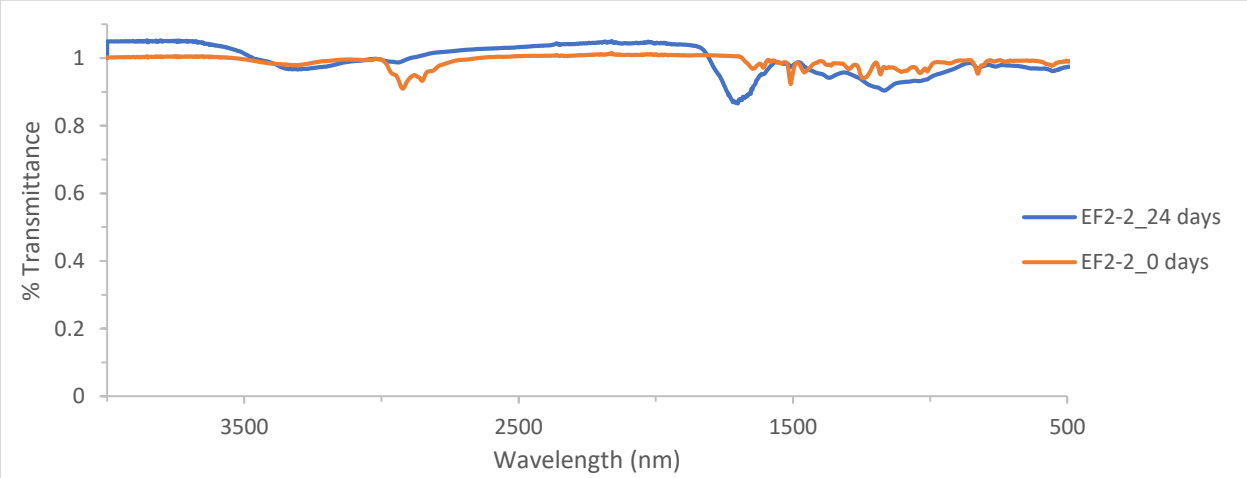

Figure A2: FTIR data for BDF formulation EF2 comparing the absorbance data initially and after 24 days of UV exposure for duplicate 2.

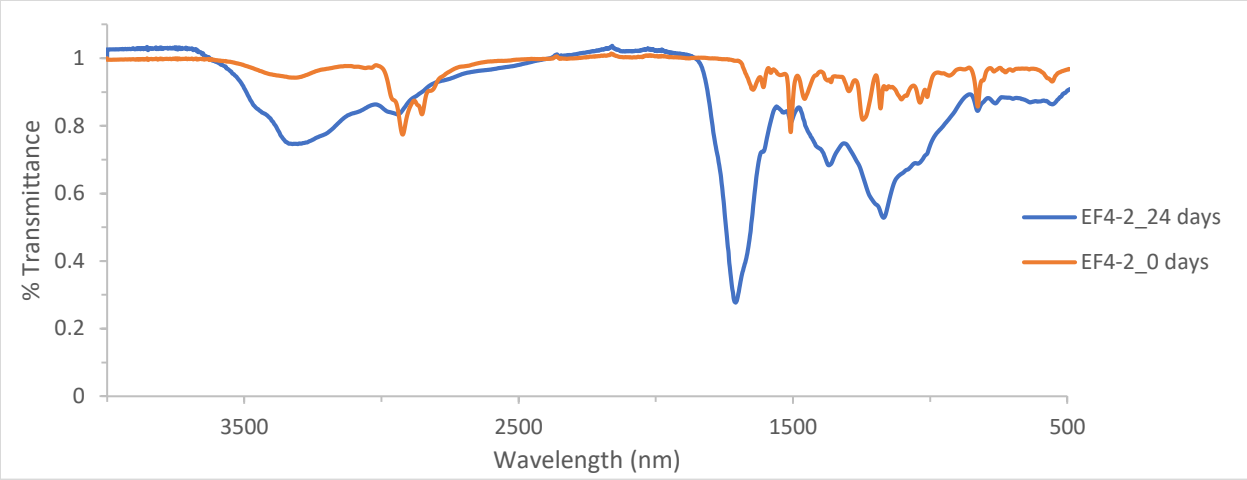

Figure A3: FTIR data for BDF formulation EF4 comparing the absorbance data initially and after 24 days of UV exposure for duplicate 2.

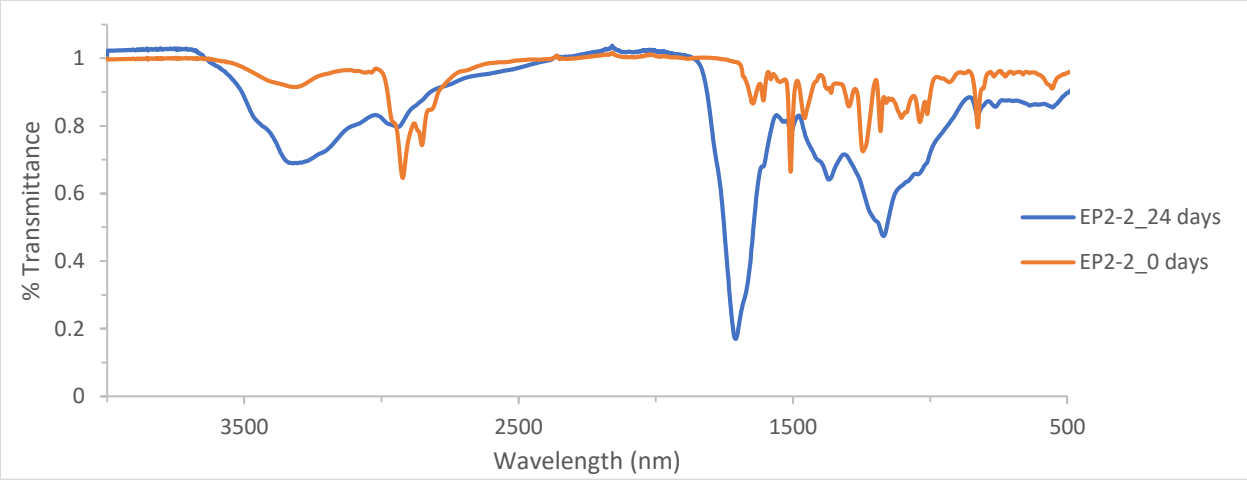

Figure A4: FTIR data for BDP formulation EP2 comparing the absorbance data initially and after 24 days of UV exposure for duplicate 2.

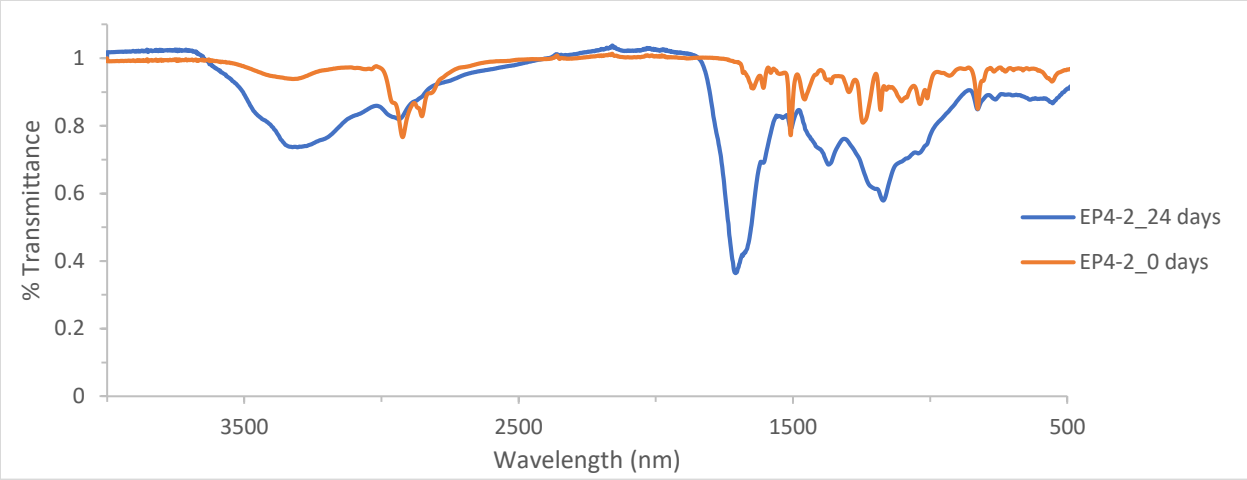

Figure A5: FTIR data for BDP formulation EP4 comparing the absorbance data initially and after 24 days of UV exposure for duplicate 2.